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DETERMINATION OF WASTEWATER ACIDS FROM CHROMIUM PLATING AND ELECTROPOLISHING SOLUTIONS

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DETERMINATION OF WASTEWATER ACIDS FROM CHROMIUM PLATING AND ELECTROPOLISHING SOLUTIONS

Samuel Sopok

ABSTRACT

The purpose of this report is to provide calibration data for the online UV-visible, conductivity, and pH detectors associated with the environmental thrust project, which is part of the Benet Laboratories vessel plating program. The chemical literature provides offline laboratory detection of chromic acid from chromium plating wastewater solutions, as well as phosphoric and sulfuric acids from electropolishing wastewater solutions. The chemical literature lacks online detection and calibration data for these wastewater acids and this is essential for the reclamation of these three acids. Not only are these chemical resources wasted if they are not reclaimed, but the U.S. Army pays increasingly more to dispose of these hazardous materials. Specific methods are illustrated here that do provide online detection and calibration of these chromium plating and electropolishing wastewater acids. These methods consist of online UV-visible, conductivity, and pH detection. These data and their associated precisions are sufficient to adequately calibrate these three detectors associated with the environmental thrust project.

KEYWORDS

Chemical Analysis, Online Calibration, Online Detection, Chromium Plating Process Solutions, Chromic Acid, Chromium Plating Wastewater Solutions, Phosphoric Acid, Sulfuric Acid, Electropolishing Wastewater Solutions, UV-visible Detection, Conductivity Detection, pH Detection, U.S. Army Environmental Thrust Project

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INTRODUCTION

The purpose of this report is to provide calibration data for the online UV-visible, conductivity, and pH detectors associated with the environmental thrust project, which is part of the Benet Laboratories vessel plating program.

The chemical literature provides offline laboratory detection of chromic acid from chromium plating wastewater solutions, as well as phosphoric and sulfuric acids from electropolishing wastewater solutions (refs 1,2). The chemical literature lacks online detection and calibration data for these wastewater acids and this is essential for the reclamation of these three acids. Not only are these chemical resources wasted if they are not reclaimed, but the U.S. Army pays increasingly more to dispose of these hazardous materials.

Specific methods are illustrated here that do provide online detection and calibration of these chromium plating and electropolishing wastewater acids. These methods consist of online UV-visible, conductivity, and pH detection.

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 2).

Chromium plating solutions typically contain 240 to 260 g/l of chromic acid, 2.4 to 3.1 g/l of sulfuric acid, 0 to 7.5 g/l of trivalent chromium, and 0 to 7.5 g/l of iron. The analytical reagent grade standard wastewater solutions used contain 25.0, 20.0, 15.0, 10.0, 5.0, and 0.0 ppm chromic acid. These wastewater solutions are at least a 1:10,000 dilution of the original chromium plating solutions.

Electropolishing solutions typically contain 640 to 730 g/l of phosphoric acid, 795 to 895 g/l of sulfuric acid, and 0 to 15 g/l of iron. The analytical reagent grade standard wastewater solutions used contain 25.0, 20.0, 15.0, 10.0, 5.0, and 0.0 ppm total acid, where total acid is from phosphoric and sulfuric acids. These wastewater solutions are at least a 1:60,000 dilution of the original electropolishing solutions. The stock solution, before the at least 1:60,000 dilution, is equivalent to a 50 percent by volume concentrated phosphoric acid and 50 percent by volume concentrated sulfuric acid solution.

UV-visible, conductivity, and pH online detectors are used for these calibration experiments in conjunction with a model DQP-1 pump (Dionex Corporation, Sunnyvale, CA). The online flowstream includes sampling from a stirred chromium plating process solution, through the pump, through the detector, and back to the stirred sample solution.

The first of these online detectors is the UV-visible variable wavelength detector (Dionex Corporation, Sunnyvale, CA). Dionex publishes a manual that is an excellent source of reference for operation and maintenance of this instrument (ref 3). In addition, a spectronic 20 UV-visible spectrophotometer (Bausch and Lomb, Inc., Rochester, NY) is used to check the online data. Bausch and Lomb also publishes a manual that is an excellent source of reference for operation and maintenance of this instrument (ref 4). Lambda maximum is 350 nm for these chromic acid wastewater solutions. Chromic acid absorbance is calibrated by an NIST method given in Reference 1.

The second of these online detectors is the conductivity detector (Dionex Corporation, Sunnyvale, CA). Dionex publishes a manual that is an excellent source of reference for operation and maintenance of this instrument (ref 5). In addition, a laboratory conductivity meter (Orion Research, Inc., Boston, MA) is used to check the online data. Orion also publishes a manual that is an excellent source of reference for operation and

maintenance of this instrument (ref 6). The full-scale of the online conductivity detector is set at 30 µS. The online conductivity detector calibrates to 147 µS using 0.00100 M potassium chloride. Chromic, phosphoric, and sulfuric acid conductance are calibrated by NIST methods given in Reference 1.

The third of these online detectors is the pH detector (Dionex Corporation, Sunnyvale, CA). Dionex publishes a manual that is an excellent source of reference for operation and maintenance of this instrument (ref 7). In addition, a laboratory pH meter (Orion Research, Inc., Boston, MA) is used to check the online data. Orion also publishes a manual that is an excellent source of reference for operation and maintenance of this instrument (ref 8). Chromic, phosphoric, and sulfuric acid pH's are calibrated by NIST methods given in Reference 1.

Using procedures in each instrument's operating manual, standard and sample solution data are recorded. Since the standard solution concentrations are known, sample solution concentrations can be calculated.

RESULTS AND DISCUSSION

The purpose of this report is to provide calibration data for the online UV-visible, conductivity, and pH detectors associated with the environmental thrust project, which is part of the Benet Laboratories vessel plating program. For each detection method, all solution readings are done in triplicate, and either the individual replicate values or their averages are reported.

Table 1 gives wavelength optimization and excellent calibration at 350 nm for wastewater chromic acid solutions by UV-visible detection. Tables 2 and 3, respectively, give standard solution calibration data and sample solution experimental data at 350 nm for wastewater chromic acid solutions by UV-visible detection. Due to a linear operating range, the following simplified calculation is used to determine the 4.4 ppm chromic acid concentration in the wastewater chromium plating sample solutions in Table 3, where the average sample absorbance is 0.066 AU:

$$\text{ppm } CrO3 = (25 \text{ ppm})(\text{sample absorbance}/0.373 \text{ AU}) \quad (1)$$

Tables 4 and 5, respectively, give standard solution calibration data and sample solution experimental data of wastewater chromic acid solutions by conductivity detection. Due to a linear operating range, the following simplified calculation is used to determine the 4.4 ppm chromic acid concentration in the wastewater chromium plating sample solutions in Table 5, where the average sample conductivity is 1.9 µS:

$$\text{ppm } CrO3 = (25 \text{ ppm})(\text{sample conductivity}/10.8 \text{ µS}) \quad (2)$$

Tables 6 and 7, respectively, give standard solution calibration data and sample solution experimental data of wastewater chromic acid solutions by pH detection. Due to a linear operating range, the following simplified calculation is used to determine the 4.0 ppm chromic acid concentration in the wastewater chromium plating sample solutions in Table 7, where the average sample pH is 4.3. Since pH is related to hydrogen ion concentration by

$$pH = - \log [H+] \quad (3)$$

and Eq. (3) becomes

$$[H+] = 10^{**}\text{-pH} \quad (4)$$

then the standard [H+] is 0.000316 M for pH = 3.5 in Table 6, and the sample [H+] is 0.000050 M for pH = 4.3 in Table 7. The sample chromic acid concentration is

$$\text{ppm } CrO3 = (25 \text{ ppm})(\text{sample } [H+]/0.000316 \text{ M}) \quad (5)$$

Tables 8 and 9, respectively, give standard solution calibration data and sample solution experimental data of wastewater phosphoric and sulfuric acid solutions by conductivity detection. Due to a linear operating range, the following simplified calculation is used to determine the 3.8 ppm total acid concentration in the wastewater electropolishing sample solutions in Table 9, where the average sample conductivity is 4.0 µS:

$$\text{ppm total acid} = (25 \text{ ppm})(\text{sample conductivity}/26.3 \text{ µS}) \quad (6)$$

Tables 10 and 11, respectively, give standard solution calibration data and sample solution experimental data of wastewater phosphoric and sulfuric acid solutions by pH detection. Due to a linear operating range, the following simplified calculation is used to determine the 3.9 ppm total acid concentration in the wastewater electropolishing sample solutions in Table 11, where the average sample pH is 4.1. The pH is related to hydrogen ion concentration by Eqs. (3) and (4), where the standard [H+] is 0.000501 M for pH = 3.3 in Table 10, and the sample [H+] is 0.000079 M for pH = 4.1 in Table 11. The sample total acid concentration is

$$\text{ppm total acid} = (25 \text{ ppm})(\text{sample } [H+]/0.000501 \text{ M}) \quad (7)$$

For the chromium plating wastewater solutions, there is at least a 1:10,000 dilution of the original chromium plating solutions. At these dilutions, only the chromic acid is detected in these wastewater solutions with no practical interference from the three other chemical species.

For the electropolishing wastewater solutions, there is at least a 1:60,000 dilution of the original electropolishing solutions. At these dilutions, only the phosphoric and sulfuric acids are detected in these wastewater solutions with no practical interference from the iron.

These data and their associated precisions are sufficient to adequately calibrate the online UV-visible, conductivity, and pH detectors associated with the environmental thrust project, which is part of the Benet Laboratories vessel plating program.

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Table 1. Wavelength Optimization (350 nm) and Calibration of Wastewater Chromic Acid by UV-Visible Detection

Wavelength (nm)	25ppm (AU)	20ppm (AU)	15ppm (AU)	10ppm (AU)	5ppm (AU)	0ppm (AU)
325	0.300	0.250	0.190	0.135	0.075	0.000
340	0.377	--	--	--	--	--
345	0.380	--	--	--	--	--
350	0.373	0.308	0.233	0.160	0.087	0.000
360	0.325	--	--	--	--	--
370	0.259	--	--	--	--	--
375	0.224	0.190	0.142	0.098	0.057	0.000
400	0.090	--	--	--	--	--
425	0.065	--	--	--	--	--
450	0.059	--	--	--	--	--
475	0.037	--	--	--	--	--
500	0.019	--	--	--	--	--
525	0.010	--	--	--	--	--
550	0.004	--	--	--	--	--
575	0.003	--	--	--	--	--
600	0.003	--	--	--	--	--
625	0.003	--	--	--	--	--

Table 2. Standard Solution Calibration Data (350 nm) of Wastewater Chromic Acid by UV-Visible Detection

Replicate	25ppm (AU)	20ppm (AU)	15ppm (AU)	10ppm (AU)	5ppm (AU)	0ppm (AU)
Standard 1a	0.373	0.308	0.232	0.160	0.087	0.001
Standard 1b	0.373	0.309	0.233	0.161	0.087	0.000
Standard 1c	0.373	0.307	0.234	0.160	0.087	0.000
X(avg)	0.373	0.308	0.233	0.160	0.087	0.000

Table 3. Sample Solution Experimental Data (350 nm) of Wastewater Chromic Acid by UV-Visible Detection

Replicate	(AU)	(ppm)
Sample 1a	0.066	4.4
Sample 1b	0.066	4.4
Sample 1c	0.065	4.4
X(avg)	0.066	4.4

Table 4. Standard Solution Calibration Data of Wastewater Chromic Acid by Conductivity Detection

Replicate	25ppm (µS)	20ppm (µS)	15ppm (µS)	10ppm (µS)	5ppm (µS)	0ppm (µS)
Standard 1a	10.8	8.8	6.7	4.8	2.7	0.2
Standard 1b	10.9	8.8	6.6	4.8	2.7	0.2
Standard 1c	10.8	8.8	6.7	4.8	2.7	0.2
X(avg)	10.8	8.8	6.7	4.8	2.7	0.2

Table 5. Sample Solution Experimental Data of Wastewater Chromic Acid by Conductivity Detection

Replicate	(µS)	(ppm)
Sample 1a	1.9	4.4
Sample 1b	1.9	4.4
Sample 1c	1.9	4.4
X(avg)	1.9	4.4

Table 6. Standard Solution Calibration Data of Wastewater Chromic Acid by pH Detection

Replicate	25ppm (pH)	20ppm (pH)	15ppm (pH)	10ppm (pH)	5ppm (pH)	0ppm (pH)
Standard 1a	3.4	3.6	3.7	3.8	4.2	5.5
Standard 1b	3.5	3.6	3.6	3.9	4.2	5.5
Standard 1c	3.5	3.6	3.7	3.9	4.2	5.5
X(avg)	3.5	3.6	3.7	3.9	4.2	5.5
[H+] (M)	.000316	.000251	.000201	.000126	.000063	.000003

Table 7. Sample Solution Experimental Data of Wastewater Chromic Acid by pH Detection

Replicate	(pH)	(ppm)
Sample 1a	4.3	4.0
Sample 1b	4.3	4.0
Sample 1c	4.4	4.0
X(avg)	4.3	4.0
[H+] (M)	.000050	---

Table 8. Standard Solution Calibration Data of Wastewater Phosphoric and Sulfuric Acids by Conductivity Detection

Replicate	25ppm (µS)	20ppm (µS)	15ppm (µS)	10ppm (µS)	5ppm (µS)	0ppm (µS)
Standard 2a	26.2	20.4	16.0	10.4	4.9	0.6
Standard 2b	26.3	20.4	16.1	10.5	5.0	0.5
Standard 2c	26.3	20.4	16.1	10.5	4.9	0.5
X(avg)	26.3	20.4	16.1	10.5	4.9	0.5

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